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PHOTODISSOCIATION OF H_2, N_2, O_2, NO, CO, H_2O, CO_2 and NH_3 IN THE EXTREME VACUUM UV SPECTRUM

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PHOTODISSOCIATION OF H_2, N_2, O_2, NO, CO, H_2O, CO_2 AND NH_3 IN THE EXTREME VACUUM UV SPECTRUM

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ABSTRACT: Photodissociations in the extreme vacuum, UV region which produce particles with energies of excitation over 8 eV, have been verified through fluorescence experiments in the Schumann UV region between 1500 and 1100 Å. The fluorescent intensities were measured as a function of the radiated wavelengths between 1000 and 645 Å.

/19*

Irradiation of H_2, O_2, NO, H_2O, CO_2 and NH_3 produces highly excited H*, O*, and N* atoms, CO* and probably H_2^* molecules. In some cases, the types of dissociation can be determined from the fluorescent intensity as a function of radiated wavelength.

The disintegration of H_2 according to $H_2 \rightarrow H(1S) + H(2P)$ begins immediately above the dissociation energy for this process.

The O_2 molecule dissociates above 14.6 eV according to

$$O_2 \rightarrow O(^3P) + O(^3S^0).$$

Disintegration probably begins at approximately 16.1 eV

$$O_2 \rightarrow O(^3P) + O(^3P).$$

The NO molecule dissociates, depending on the radiated wavelength, forming highly excited O* or N* atoms. Dissociation takes place between 16.0 and 16.8 eV

$$NO \rightarrow N(^4S) + O(^3S^0)$$

In the range from 16.8 to 18.3 eV, dissociations to highly excited N atoms have been verified, and at 17.25 eV, the disintegration

$$NO \rightarrow N(3s^4P) + O(^3P);$$

Above 18.4 eV, there are two possibilities

$$NO \rightarrow N(^2D^0) + O(^3S^0) \quad \text{and} \quad NO \rightarrow N(^4S) + O(^4S^0).$$

There is dissociation of H_2O

$$H_2O \rightarrow OH(X^2\Pi) + H(2S, 2p)$$

which results in the emission of the L_a line.

The fluorescences in the case of CO_2 and NH_3 are probably caused by

$$CO_2 \rightarrow CO(A^1\Pi) + O(2^1D)$$

or $NH_3 \rightarrow NH_2 + H\ (n \geq 2)$ and/or $NH_3 \rightarrow NH + H_2(^1\Sigma_u^+)$

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*Numbers in the margin indicate pagination in the foreign text.

In the far vacuum UV region ($\lambda < 1000$ Å), in addition to photo-ionization, dissociation processes occur to a noticeable extent in numerous bi- and poly-atomic molecules. This has been established by measurements of the total absorption cross section σ_{tot} and the ionization cross section of Weissler, et al. The difference σ_{ion} is often several eV above the first ionization potential only in the discrete segment of an absorption spectrum, i.e., in the long-wave range.

Only in very simple cases, e.g. H_2, is it possible, in the extreme UV region, to determine the dissociation process in detail from the absorption spectrum of the mother molecule, i.e. the excitation states of the disintegration products in addition to their chemical nature [1-5]. Even in the case of somewhat more complicated molecules such as O_2 and NO, the absorption spectrum provides no clear indication, since usually several combinations of atomic states /20
correspond to a highly excited molecular level according to the correlation rules. Besides that, the absorption spectrum in the short-wave UV region usually consist of a single more or less structured continuum or of overlapping systems of diffuse bands.

Those dissociations which lead to electronically excited, nonmetastabile particles, can be investigated using fluorescence spectra. In this case, there is a definite possibility of also determining the dissociation cross section by measuring the intensity. If the quantum energy is much higher than the dissociation energy of the initial state, we can assume that the dissociation energy of most molecules is much less than 10 eV, a large number of the dissociations in the far UV region can be verified using fluorescence experiments.

Fluorescence experiments were carried out quite some time ago by Wood [6], Oldenberg [7], McLennan, Ruedy and Clements [8]. H_2, O_2, N_2, CO and H_2O were irradiated with the undispersed light from spark discharges, and the fluorescence spectra were recorded spectrographically in the visible and near UV regions of the spectrum. When H_2, O_2 and H_2O are irradiated, some atomic lines from H and O occurred as well as bands of the molecular spectra in the in the case of N_2 and CO. These tests do not preclude the possibility of secondary excitation of atoms which originate primarily in the initial state. Beside that, experiments with undispersed radiation do not permit measurement of the initial energies of the disintegration processes and their relative

frequency. Meyer carried out the first experiments with monochromatic light [9].

Recently, Schoen, Judge and Weissler [10] investigated the formation of electronically excited ions, (N_2^{+**}, O_2^{+**}, CO^{+**}) when N_2, O_2 and CO are ionized with monoenergetic radiation between 500 and 1000 Å. They verified the excitation through total fluorescence between approximately 3500 and 5500 Å photoelectrically. More detailed investigations of excited N_2^{+**} states were carried out by Huffman, Tanaka and Larabee [11] using a light source with a continuous spectrum and a monochromator.

The subject of this work was photodissociations of H_2, N_2, O_2, NO, CO, H_2O, CO_2 and NH_3 below 1000 Å. A light source was used, which emitted 20 lines with sufficient intensity between 645 Å and 1000 Å. A monochromator was used to filter out a line and the fluorescence intensity was measured integrally in the ranges 1100 to 1250 Å and 1250 to 1500 Å. Thus, the portion of the dissociations which occur between 645 and 1000 Å and generate the particles with excitation energies above 8.26 eV $\triangleq$ 1500 Å is verified. The fluorescence was measured in the vacuum UV region because the resonance transitions with the longest waves of the possible disintegration products, H, N, O, H_2, N_2 and CO, occur in this region.

1. Experimental Portion

The measurement apparatus is shown schematically in Figure 1. The light source was a capillary spark discharge in air with a pressure of several 10^2 to 10^1 torr[10]. The quartz capillary tube K had a diameter of 1.5 mm and a length of 40 mm. When the pressure in the spark gap and the voltage at condenser C are adjusted properly, we obtain a constant number of discharges in each negative half-wave. All measurements were made with 13 discharges per period (50 Hz) at a breakdown voltage of 1.5 kV and a capacitance of 0.04 μF. /21 Figure 2 gives the voltage curve at the spark gap.

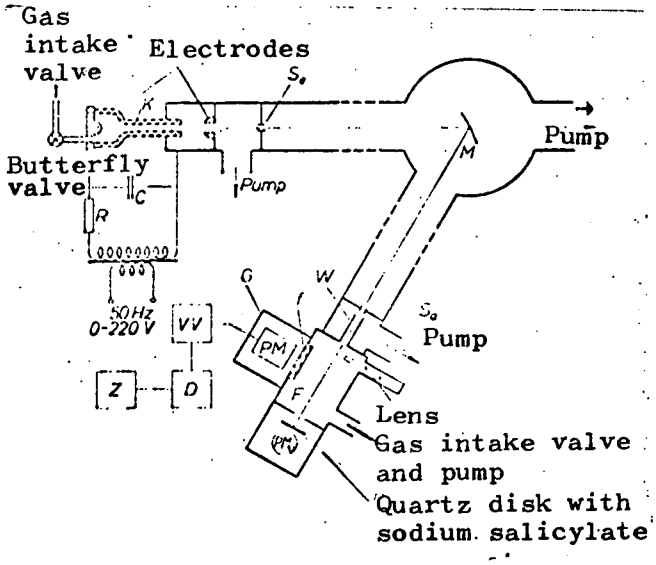


Figure 1. Measurement apparatus.

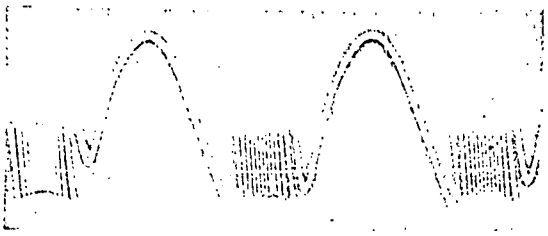


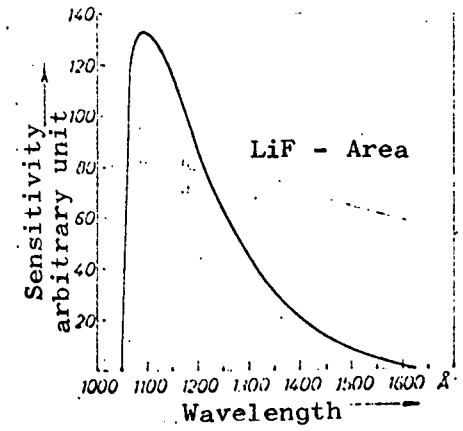
Figure 2. Voltage curve at the spark gap.

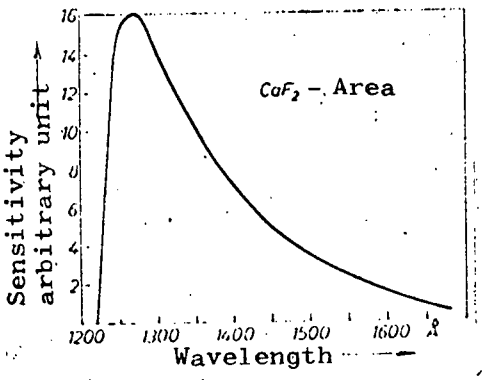
The pressure in front of the entrance slit S_e and behind the exit slit S_a of the monochromator M (1-m-Seya-Namioka) was 10^{-3} torr, and 10^{5} torr in the monochromator itself. In the fluorescence chamber F, the gases could be continuously fed to the apparatus through the throttle D up to pressures of 10^{1} torr without essentially increasing the pressure in the monochromator itself. A groove-shaped channel W served as a flow resistance.

The entrance and exit slits were 0.2 mm wide and 10 mm long. Since the lattice for a wavelength of 1500 Å was blazed, the measurements were taken in the second order. The intensity of the second order was larger than that of the first order by a factor of approximately 20. The band width was 1.5 Å. In this case, 10^{6} to 10^{7} quanta/sec entered the fluorescence chamber per line, as was shown with the Bendix multiplier (type M-306) [12]. The relative intensities i_0 (λ_0) of the radiated lines were measured with a sodium salicylate sensitized multiplier (PM_0) mounted behind the chamber F.

In order to measure the intensity of the fluorescent radiation, a multiplier (Bendix M-306) was used, which is sensitive only to quanta above approximately 8.26 eV $\triangleq$ 1500 Å, and has a dark current of 10^{20} Å at room temperature, when the amplification factor is 10^{7}. The multiplier housing G was hermetically sealed through window f facing the fluorescence chamber F and the pressure reduced to 10^{-6} torr. The two measurement ranges 1100-1500 Å and 1250-1500 Å were covered with windows of LiF and CaF_2. According to the measurements of Hunter [12] the yield of the photocathode is approximately 2×10^{-3} electron/quantum at 1500 Å. At 1100 Å, it rises almost exponentially to 5×10^{-2} electron/quantum. Figures 3 and 4 give the relative spectral sensitivity of the multiplier with the windows used. In order to determine the sensitivity, the transmission of the windows was measured as a function of the wavelength and multiplied by the photo-yield of the multiplier.

If we select an effective cross section σ_D of 1000 cm^{-1} and a pressure of 10^{-1} torr in the fluorescence chamber, and assume that σ_D is conditioned only by dissociations within the measurement range of 1100-1500 Å, then we find, when the incoming current in the fluorescent chamber is 10^{6}-10^{7} quantum/sec,





Figures 3 and 4. Relative sensitivity of the multiplier (Bendix M-306) with previously connected LiF (3) or CaF_2 (4) window.

that a maximum of 10^4 fluorescence quanta per second impinge on the 2 x 2 cm^2 cathode of the multiplier, which is located 5 cm from the center of the fluorescence chamber through the window, without taking the absorption into account. Taking the electron yield into account, the electron current at the cathode would be approximately 100 electrons per sec. However, tests show that the actual fluorescent intensities were at least one order of magnitude smaller. For this reason, the measurements were made with a counter Z.

The impulses which impinge on the multiplier anode, and which are statistically distributed in height, were trimmed behind a preliminary amplifier (VV) by a discriminator (D) to such an extent that the average number of the substratum pulses at the output of the counter was Z_U = 2 pulses/min. This substratum was not affected by whether light entered the fluorescent vacuum chamber or not. /22

It also does not change when gases such as Ar, CO, N_2 are allowed to enter the chamber, in which case no fluorescence is expected between 1100 and 1500 Å for a radiation between 900 and 650 Å (see below).

2. Results and Discussion

The number of impulses in the wavelength ranges 1100 to 1500 Å and 1250 to 1500 Å, which strike during Δt minutes, was measured at wavelengths λ_0 and for constant pressure p. The average number of substratum impulses $Z_U = 2\ \Delta t$ is subtracted from this number thereby giving us fluorescence counts $Z_L(\lambda_0)$, $Z_C(\lambda_0)$ for LiF and CaF_2 ranges. $Z_L(\lambda_0)$ and $Z_C(\lambda_0)$ are referred to the relative intensities in the fluorescence chamber $i(\lambda_0)$ for wavelength λ_0. $i(\lambda_0)$ is measured with the multiplier MP_0 and remained constant at ±7% for all tests. In order to be able to compare the fluorescence intensities of the molecules

for the same fluorescence spectra, even with each other, the magnitude $Z_L(\lambda_O)/i(\lambda_O)$ and $Z_C(\lambda_O)/i(\lambda_O)$ are reduced to equal pressures and equal count times. These reduced fluorescence intensities, designated in the following as I_L and I_C are shown in the figures in conventional units, in which case, the fluorescence intensity of hydrogen is set at 100 for λ_O = 833 Å in order to standardize the results. The errors I_L and I_C, the limits of which are indicated in the figures, are obtained for the most part from the statistical error in the counts and the fluctuations in the light intensity $i(\lambda_O)$ during Δt. The count times were 5 to 30 minutes depending on the fluorescence intensity per line.

I_L and I_C are average values of the intensity distribution of the fluorescence spectra in the two measurement ranges and are functions of the spectral sensitivity distribution of the measurement apparatus according to Figures 3 and 4.

Besides the fact that I is a function of the wavelength, the count Z_L was measured as a function of the pressure for a wavelength λ_O (Figures 5, 6, 7 and 8). The deviations from the linear slope at higher pressures are caused by extinguishing processes or the reduction in the amount of radiated light as a result of preliminary absorption up to the center of the fluorescence chamber.

The number of impulses, which lie above the threshold of discrimination, i.e. the count Z (imp/Δt) is proportional to the number of quanta which impinge on the cathode as a result of the statistical impulse amplitude distribution. The necessary precondition that Z be considerably less than the number of light pulses during the count period Δt, was satisfied in all the tests. The proportionality between Z and the fluorescence intensity is experimentally confirmed by the linear rise in the count along with the pressure in the fluorescence chamber (Figure 5-8). Deviations from the linearity at higher pressures are caused by the above-mentioned factors. $I_L(\lambda_O)$ and $I_C(\lambda_O)$ were measured at pressures within the linear range.

The fluorescence intensities I_L and I_C were measured at each of the 20 lines which were below 1000 A. In the figures, only the range from approximately 900 Å is contained, because none of the molecules exhibited fluorescence between 1000 and 900 Å.

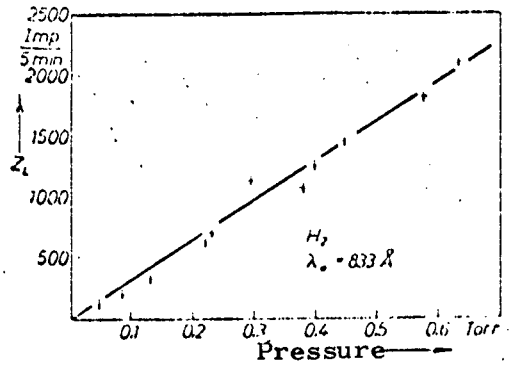


Figure 5. The count as a function of the pressure for H_2 (λ_0 = 833 Å).

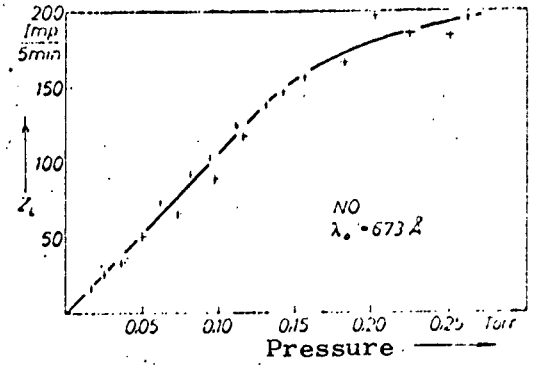


Figure 6. The count as a function of the pressure for NO (λ_0 = 673 Å).

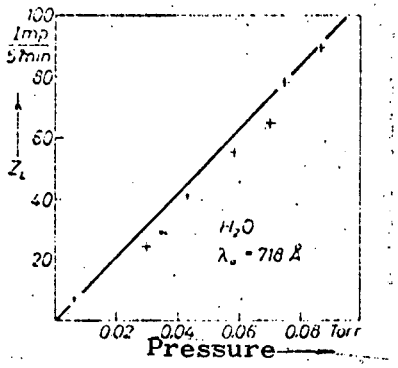


Figure 7. The count as a function of the pressure for H_2O (λ_0 = 718 Å).

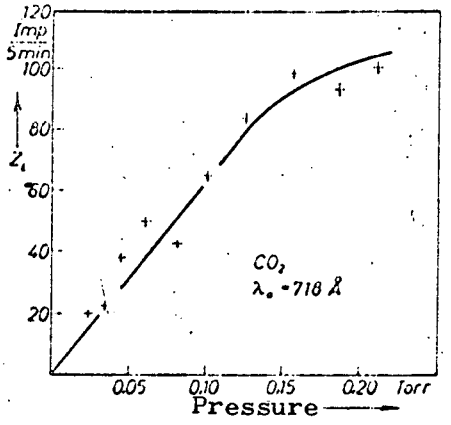


Figure 8. The count as a function of the pressure for CO_2 (λ_0 = 7.8 Å).

H_2

On the basis of the heavy expansion of the lines in the bands $v' \geqq$ of the $^1\Pi_u \leftarrow {}^1\Sigma_g^+$* system, beginning at 849 Å, and the continuum, which also begins at 849 Å, we can see from the absorption spectrum that, at this wavelength, the disintegration /23

$$H_2(^1\Sigma_g^+) \rightarrow H_2(^1\Pi_u) \rightarrow H(1S) + H(2P) \quad (\lambda \lesssim 849\ \text{Å}) \qquad (1)$$

is initiated through predissociation [1, 2, 4, 5]. Even below the ionization threshold (803.7 Å ≙15.4 eV), dissociation processes must still occur according to the measurements of Weissler, et al. [3, 14].

The process (1) leads to the fluorescence of the L_α-line. The fluorescence spectrum of decays with more highly excited H.atoms ($n \geqq 3$) can, depending on the

* Translator's Note: Text is blurred. Notations are as accurate as copy permits.

wavelength L_α-, contain other Lyman lines and lines of the longer wave H series, in addition to the λ_0 line.

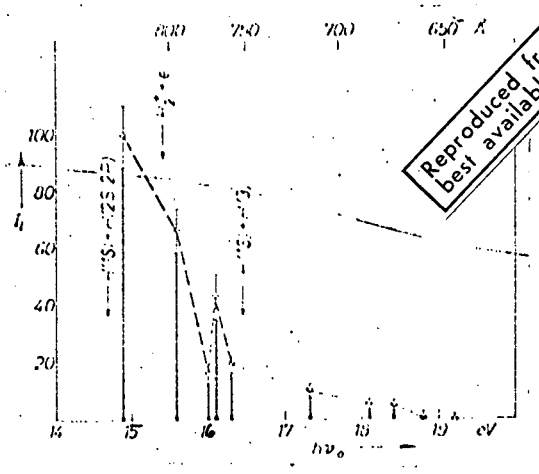


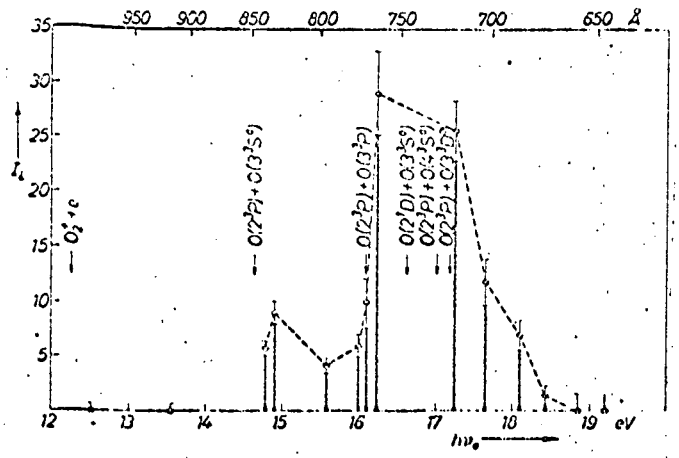
Figure 9. Fluorescence intensity for H_2 in the LiF range.

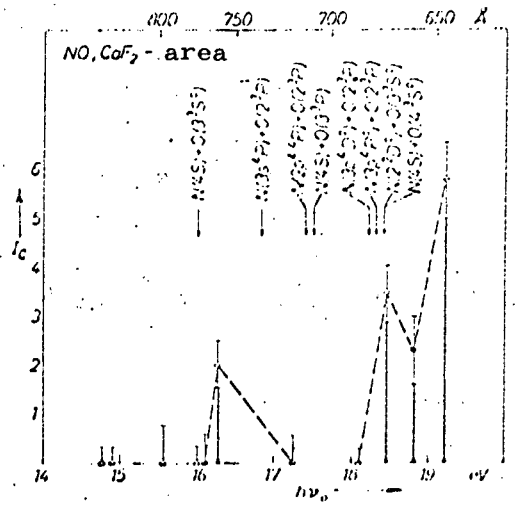
Figure 9 shows the fluorescence intensity I_L as a function of λ_0. The intensities are ascribed exclusively to the lines, since, for example, the L_u- and the H_α-lines, which must appear when there is disintegration to $H(1S) + H(n \geqq 3)$, are outside the measurement range. For this reason, only that part of the fluorescence of the more highly excited H atoms ($n \geqq 3$) is measured, which leads to the L_u line via cascades. Thus, there is agreement with the fact that no fluorescence could be found in the CaF_2 range. As further verification, a test was made in which the fluorescence chamber was set up in front of the entrance slit, and the gas was irradiated with the undispersed light from the spark. When the spectrum was recorded through the LiF window, only the L_u-line appeared as expected.

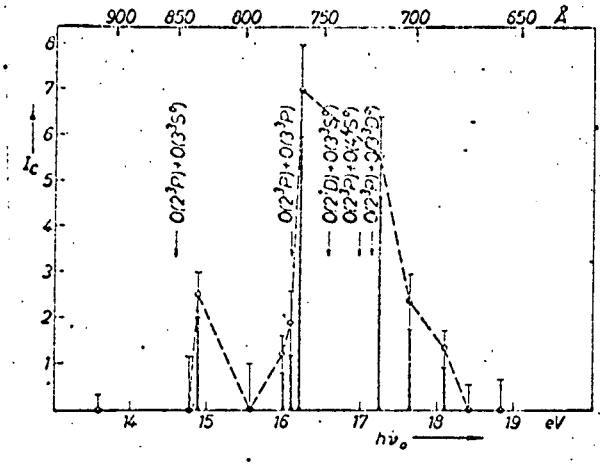
The intensity maximum at 16.1 eV is conspicuous. This is explained by the fact that these lines lie right in the strong, diffuse 1-0 level of vibration of the $^1\Pi_u$-state, whereas all other lines lie in the regions with weaker absorption between the bands of the $^1\Pi_u \leftarrow {}^1\Sigma_g^+$ system. By using a light source with a continuum, it can be expected that other structures will appear in the intensity distribution of the fluorescence spectrum, which would make a more exact analysis of the dissociation processes possible.

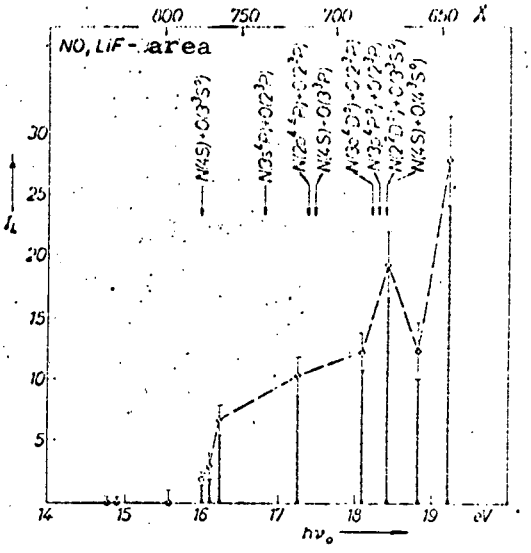
O_2

Theoretically, O_2 has so many dissociation possibilities in the far vacuum UV region that a definite determination of the actually occurring disintegrations through analysis of the absorption spectrum consisting of continuum and numerous diffuse bands is hardly possible. Of the highly excited molecular states, a /24
$^3\Pi_u$-level has already been identified by Huber [15] on the basis of the absorption spectra recorded by Price and Collins [16], Tanaka and Takamine [17],









Figures 10 and 11. Fluorescence intensity for O_2 in the LiF range (10) and the CaF_2 range (11).

Figures 12 and 13. Fluorescence intensity for NO in the LiF range (12) and in the CaF_2 range (13).

from which there are transitions to the ionization continuum, and which can be constructed according to the correlation rules from combinations of the atomic states $2^3P + n^5S^0$ and $2^3P + n^3S^0$. Whether the corresponding dissociations occur along with ionization has not yet been investigated. It can be assumed that dissociation processes occur on the basis of the absorption and ionization measurements of Lee and Weissler [18] and the tests of McLennan, Ruedy and Clements [8].

The intensities I_L and I_C show the same relative intensity curve (Figures 10 and 11); the ratio I_L/I_C is approximately 4/1 and is equal to the permeability

ratio of the LiF and CaF_2 windows at approximately 1300 Å. From this we can conclude that the fluorescence spectrum exhibits no lines between 1100 Å and 1250 Å. This agrees with the fact that there is a permissible transition of the O atom, namely $3^3S^0 \rightarrow 2^3P$ at 1305 Å only in the CaF_2 range. Since the 3^5S^0-state is metastabile, a fluorescence of the intercombination transition $3^5S^0 \rightarrow 2^3P$ can be ignored, i.e. a statement can be formulated on dissociations where O atoms are produced in the quintet system. The measured intensities must be assigned to these processes, in which O atoms are formed either directly in the 3^3S^0-state or in states which combine with 3^3S^0. /25

Figures 10 and 11 give all the possibilities for disintegration which could be considered a cause of the intensities, with their given energies of dissociation. The fluorescence begins slightly above the process with the lowest energy of dissociation:

$$\begin{aligned} O_2 &\rightarrow O(2^3P) + O(3^3S^0), \\ O(3^3S^0) &\xrightarrow{1305\,\text{Å}} O(2^3P). \end{aligned} \qquad (2)$$

This dissociation takes place at least up to 770 Å, this dissociation energy of the next possible process $O(2^3P) + O(3^3P)$, and originates according to Huber [15] in the $^3\Pi_u$-level. Since the intensity jumps sharply at approximately 770 Å, it can be assumed that there the dissociation

$$\begin{aligned} O_2 &\rightarrow O(2^3P) + O(3^3P), \\ O(3^3P) &\xrightarrow{8446\,\text{Å}} O(3^3S^0) \xrightarrow{1305\,\text{Å}} O(2^3P) \end{aligned} \qquad (3)$$

begins. McLennan, Ruedy and Clements observed the 8446 Å-line [8] which, however, could also be caused by transitions from higher states.

Disintegration (2) and (3) obviously do not occur at repulsion levels, but rather as a result of the transition from highly excited levels to the continuum, since the fluorescences begin directly above the dissociation energies.

The relatively high intensity at 735 Å agrees with the theory of Lee and Weissler [18] that the absorption continuum which begins at 740 Å is determined not only by ionization but to a great extent also by dissociations.

NO

In the case of NO, several highly excited molecular levels have been identified by Tanaka [19], Huber [20] and Astoin [21], which can, in part, be classified in Rydberg series and lead to molecular ion states. According to the measurements of Sun, Walker and Weissler [22] it is suspected that dissociations

also occur along with transitions to the ion.

If the molecule disintegrates while forming excited O atoms, then, analogous to O_2, those disintegrations are observed which lead to the emission $3^3S^0 \rightarrow 2^3P$ (1305 Å). As regards the N atom, the LiF range contains the two transitions $3s^4P \rightarrow 2^4S^{10}$ and $2p^4P \rightarrow 2^4S^0$ at 1200 and 1134 Å respectively, i.e. disintegrations are measured which directly or indirectly yield $N(3s^4P)$ and $N(2p^4P)$. Dissociations to quintet O atoms and doublet N atoms cannot be noticed, practically speaking, in the fluorescence spectrum, since the intercombinations are too weak.

The comparison between Figures 12 and 13 shows that the intensities in the LiF range at 17.25 eV and at 18.4 eV in the CaF_2 range do not occur and that the intensities for the other lines are weakened to a ratio of merely 4 to 1, analogous to O_2. From this, it can be concluded that dissociations occur at low and high quantum energies, which lead to highly excited O atoms, and at intermediate quantum energies, which lead to highly excited N atoms.

The dissociation begins with the lowest energetic process.

$$\begin{array}{l} NO \rightarrow N(^4S) + O(3^3S^0), \\ O(3^3S^0) \xrightarrow{1305\ \text{Å}} O(3^3S^0) \end{array} \qquad (4)$$

since the fluorescence at 16.0 to 16.3 eV can only be assigned to this process. It is followed by the dissociation

$$\begin{array}{l} NO \rightarrow N(3s^4P) + O(2^3P), \\ N(3s^4P) \xrightarrow{1200\ \text{Å}} N(^4S) \end{array} \qquad (5)$$

to which the emission in the LiF range at 17.25 eV must correspond. The intensity at 18.1 eV can, in addition to (5), also be caused by the dissociation

$$\begin{array}{l} NO \rightarrow O(2^3P) + N(2p^4P), \\ N(2p^4P) \xrightarrow{1134\ \text{Å}} N(^4S) \end{array} \qquad (6)$$

The process

$$\begin{array}{l} NO \rightarrow N(^4S) + O(3^3P), \\ O(3^3P) \xrightarrow{8446\ \text{Å}} O(3^3S^0) \xrightarrow{1305\ \text{Å}} O(2^3P) \end{array} \qquad (7)$$

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with a dissociation energy of 17.4 eV, however, does not take place in this range, since the corresponding fluorescence, which must occur in the CaF_2 range, does not appear.

Above 18.43 eV, the dissociations again favor excited O atoms, since the intensities at 18.4, 18.8 and 19.2 eV both in the LiF and CaF_2 range occur in the ratio of 4 to 1. The emission beins in the CaF_2 range directly above the dissociation energy of $N(2^2D) + O(^3S^0)$ and $N(^4S) + O(4^3S^0)$, i.e.

$$\begin{aligned} &NO \rightarrow N(2^2D) + O(3^3S^0), \\ &O(3^3S^0) \xrightarrow{1305\ \text{Å}} O(2^3P) \end{aligned} \qquad (8)$$

and/or

$$\begin{aligned} &NO \rightarrow N(^4S) + O(4^3S^0), \\ &O(4^3S^0) \begin{cases} \rightarrow O(2^3P) \\ \xrightarrow{8446\ \text{Å}} O(3^3P) \xrightarrow{1305\ \text{Å}} O(3^3S^0) \xrightarrow{1305\ \text{Å}} O(2^3P) \end{cases} \end{aligned} \qquad (9)$$

can occur.

The dissociations $N(3p\,^4D^0) + O(2^3P)$ and $N(3p\,^4P^0) + O(2^3P)$, which lead to excited N atoms, with dissociation energies of 18.22 and 18.32 eV respectively can be excluded since they would merely yield emissions in the LiF range.

According to Huber [20], the excited state $O_2(^2\Sigma^+)$ must be assumed for disintegration (4), which at the same time leads to the molecular ion $O_2^+(a^3\Sigma^+)$. Disintegration (5) initiates presumably either from $O_2(^2II)$ or from a previously unidentified state [20].

H_2O

There are three disintegration possibilities

$$H_2O \rightarrow H_2 + O^*, \qquad (10)$$
$$H_2O \rightarrow H_2^* + O, \qquad (11)$$
$$H_2O \rightarrow H^* + OH \qquad (12)$$

which must be discussed, in which case O*, as in the case of O_2, means excited triplet atoms, H*, excited H atoms ($n \geq 2$) and H_2^* electronically excited H_2 molecules of the singlet system.

With the disintegration to $H_2 + O^*$, the 1305 A- O-line, i.e. a fluorescence in the CaF_2 range, must occur, which was, however, not observed. The fluorescence lies exclusively in the LiF range (Figure 14), whereby process (10) can be eliminated.

Dissociation (11) would lead to emission of the H_2 system $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$, the bands of which lie in the LiF and in part also in the CaF_2 range [23]. The lack of fluroescence in the CaF_2 range shows that (11) is not possible. Besides that, the process is also very improbable when the rule of spin is taken into

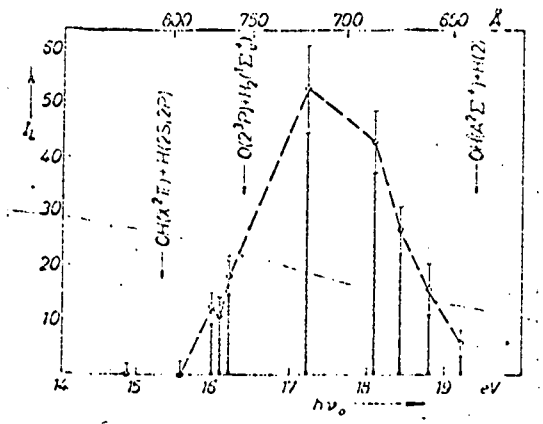

Figure 14. Fluorescence intensity for H_2O in the LiF range.

account.

$$H_2O \rightarrow O(2^3P) + H_2(^1\Sigma_u^+) \qquad (11a)$$

since the absorption occurs primarily from the $^1A_1$ initial state of the H_2O to the excited singlet levels.

The rules of spin would permit the formation of $O(2^1D) + H_2(^1\Sigma_u^+)$, however. But this disintegration requires a quantum energy of at least 18.14 eV and thus is, in no case, able to explain the strong fluorescence in the case of long-wave radiation. For this reason, it must be assumed that the total fluorescence is produced by the dissociation

$$H_2O \rightarrow OH(X^2\Pi) + H(n \geq 2) \qquad (12a)$$

In this case, the OH radical can still only be excited by vibration and rotation, since the formation of an H(2S, 2P), and an OH radical in the first excited electron level $A^2\Sigma^+$ would require a quantum energy of more than 19.4 eV.

CO_2

The CO_2 absorption spectrum, between 600 and 900 Å, consists of numerous, in part, diffuse bands and three continua. The two continua, which begin at 860 and 690 Å respectively, are ascribed to ionizations [24-27]. Rathenau /27 suggests that dissociations occur in the third narrow continuum at 760 Å [25].

Figure 15 shows the fluorescence intensity in the LiF range. In the case of the strongest intensities (16.0 and 17.25 eV), a weak fluorescence could also be measured in the CaF_2 range. Its intensity is also included in Figure 15.

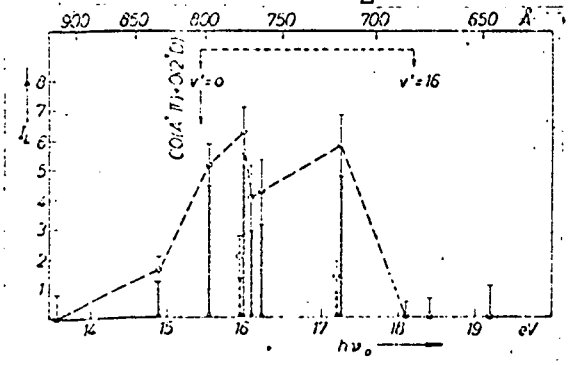

Figure 15. Fluorescence intensity for CO_2 in the LiF range.

The fluorescence can only correspond to disintegrations in O and CO since dissociation in C and O_2 is not possible with excitation energies of at least 8.26 eV $\triangleq$ 1500 Å when the photo-energies are less than 19.2 eV, since $D(C\text{-}O_2) = 11.46$ eV. Assuming that the absorption of the CO singlet initial state leads mainly to excited singlet levels, and that the disin-

tegrations occur from them, the most probable processes could be restricted using the Wigner spin rules, to those in which singlet-singlet and triplet-triplet combinations of CO and O are produced [28]. If we take into consideration that the maximum photo-energy is 19.2 eV, then the dissociations $CO(A^1\Pi)$ + $O(2^1D)$ and $CO(a^3\pi, a'^3\Sigma^+, d^3\Delta, c^3\Sigma^-, b^3\Sigma^+)$ + $O(2^3P)$ could be possible. Since the intercombination transitions in the case of CO are weaker by a factor of approximately 10^3 than the fourth system $A^1\Pi \rightarrow X^1\Sigma^+$[29], it can be assumed that the fluorescence is mainly the result of the dissociation

$$\begin{aligned} CO_2 &\rightarrow CO(A^1\Pi) + O(2^1D), \\ CO(A^1\Pi) &\rightarrow CO(X^1\Sigma^+) + h\nu' \end{aligned} \qquad (13)$$

However, other processes must also be possible, since the intensity at 14.9 eV cannot be explained by (13). Probably the precondition that only excited singlet levels be reached through the absorption, is not completely met, since there are singlet-triplet transitions in the case of longer wavelengths [30].

NH_3

The NH_3 was irradiated at a pressure of 0.14 torr. In the LiF range, weak but definitely verifiable fluorescence intensities occurred at 15.55 and 17.25 eV.

Since the fluorescence can only be caused by excited H atoms ($n \geq 2$) and/or H_2 molecules in the $^1\Sigma_u^+$ state, the possibilities for disintegration are

$$NH_3 \rightarrow NH_2 + H(n \geq 2) \qquad (14)$$

and/or

$$NH_3 \rightarrow NH + H_2(^1\Sigma_u^+). \qquad (15)$$

Further investigations are needed for a more exact description.

N_2, CO, N_2O

Irradiation of these molecules produced no verifiable fluorescence. This is expected in the case of N_2 and CO, since the dissociation energy of N_2 is 9.76 eV and the excitation of the N line $3^4P \rightarrow 2^4S^0$ with the longest verifiable wavelength requires 10.31 eV. If dissociation to a non-excited and a highly excited N atom is possible, it can only occur above 20.08 eV.

In the case of CO, the sum of the dissociation energy D(CO), 11.11 eV and the required fluorescence energy H r, 8.26 eV, is also greater than the energy of the line with the shortest wavelength (19.2 eV).

The dissociation energies of N_2O in the initial state are

$D(N - NO)$ 4.5 eV and $D(N_2 - O)$ 4.3 eV[31].

Thus, the energy of the radiated quanta would suffice for dissociation and simultaneous excitation of N, O, and N_2 above 8.26. But obviously, these processes are not possible, or very improbable since no fluorescence occurs. /28

The lack of fluorescence in N_2, CO, N_2O is important for measurement technology since this shows that the fluorescences established for the other molecules are not contaminated by light with a longer wavelength, which could have entered the fluorescence chamber and impinged on the multiplier cathode as scattered radiation. The previous tests with undispersed light [6, 8] showed in certain cases the resonance spectrum of the irradiated molecules.

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